PB86-244746

In-situ Treatment of Hazardous Waste Contaminated Soils

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Prepared for

Environmental Protection Agency, Cincinnati, OH

Aug 86

U.S. Department of Commerce
National Technical Information Service
NTIS

PB86-244746

EPA/600/D-86/196
August 1986

IN-SITU TREATMENT OF HAZARDOUS WASTE CONTAMINATED SOILS

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U.S. DEPARTMENT OF COMMERCE
NATIONAL TECHNICAL
INFORMATION SERVICE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA/600/D-86/196	2.
3. RECIPIENT'S ACCESSION NO. PB86-244746/AS	
4. TITLE AND SUBTITLE IN-SITU TREATMENT OF HAZARDOUS WASTE CONTAMINATED SOILS	5. REPORT DATE August 1986 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) R. Sims and K. Wagner	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS JRB Associates, 8400 WestPark Dr., McLean, VA 22102 Utah Water Research Laboratory, Utah State University, Logan, Utah	10. PROGRAM ELEMENT NO. TEJY1A 11. CONTRACT/GRANT NO. EPA - 68-03-3113
12. SPONSORING AGENCY NAME AND ADDRESS Water Engineering Research Laboratory Office of Research and Development U. S. Environmental Protection Agency Cincinnati, OH 45268	13. TYPE OF REPORT AND PERIOD COVERED Research Paper-6 months 14. SPONSORING AGENCY CODE EPA/600/14

15. SUPPLEMENTARY NOTES

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Cincinnati, OH 45268

16. ABSTRACT

Techniques were investigated for in-situ treatment of hazardous wastes that could be applied to contaminated soils. Included were chemical treatment methods, biological treatment, photochemical transformations and combination methods. Techniques were developed based on fundamental principles of soil science and hazardous waste management.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS (This Report) UNCLASSIFIED 20. SECURITY CLASS (This page) UNCLASSIFIED	21. NO. OF PAGES 26 22. PRICE $9.95

EPA Form 2220-1 (9-73)

NOTICE

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INTRODUCTION

Uncontrolled disposal of hazardous wastes frequently results in the production of large quantities of contaminated soils. It is often cost prohibitive or impractical to excavate, haul and dispose of these soils in an approved landfill. In-situ treatment of these soils is being investigated in this project as an alternative to excavation and disposal. The approach to treating soils is based on: (1) fundamental soil chemical, physical, and biological processes, (2) methods developed for land treatment of industrial wastes, and (3) hazardous waste land treatment (HWLT) regulations recently promulgated in 40CFR, part 264, 1983. The goals of in-situ management include treating contaminated soils until an acceptable level is achieved, and protecting groundwater and surface water resources without physically removing or isolating the contaminated soil from the contiguous environment.

TECHNICAL GUIDANCE MANUAL

The results of this paper study will be presented in a two-volume manual titled, "In-Situ Treatment Techniques Applicable to Large Quantities of Hazardous Waste Contaminated Soils." The manual is being

developed and this paper presents its projected contents. Volume one will contain flow charts, decision trees, procedures, and quantitative and qualitative criteria for determining treatment feasibility and selecting treatment processes and combinations of processes. Characterization of site specific conditions requires information concerning soil, site, and waste parameters in order to assess the behavior and fate of chemical-soil interactions using qualitative and quantitative models. Based on the results obtained, treatment needs can be identified and prioritized with respect to: (1) potential migration to groundwater and surface water, and to the atmosphere, and (2) recalcitrance, toxicity, and persistence in soil systems.

Specific in-situ treatment options will be selected based on the following factors: (1) waste characterization, (2) matching of waste constituent properties and treatment techniques, (3) safety considerations (4) analysis of the suitability of soil for treatment, and (5) economic analysis. Waste characterization includes chemical class, concentration, and behavior in soil systems. Matrices will be developed to match specific treatment techniques with waste constituents. Complex wastes will be constructed from individual constituents present in the wastes, and treatment techniques will be evaluated for individual constituents as well as complex wastes. Finally, verification procedures to determine in-situ treatment effectiveness will be suggested. The verification procedures include: (1) groundwater sampling, (2) soil core/soil pore sampling, and (3) monitoring of soil macrostructure characteristics.

Volume two will contain specific information concerning in situ treatment technologies and soil-waste interactions. A discussion and

summary of specific physical, biological, chemical, and photochemical treatment techniques applicable for in situ treatment will be presented. For each treatment process, factors addressed will include the achievable level of treatment, secondary impacts of using the treatment technique, monitoring treatment performance, equipment needs and application methods, and costs. Combinations of processes into treatment trains will also be considered. The final section of volume two will contain specific information concerning the characterization and evaluation of fundamental processes in soil-waste systems that affect the feasibility and effectiveness of in-situ treatment.

The two-volume manual will be prepared for engineers and managers to select and apply in-situ treatment technologies. Since the majority of in-situ treatment technologies presently available for hazardous wastes have not been thoroughly field tested, this manual will present promising techniques based on laboratory and field results with hazardous and nonhazardous wastes. Also, the manual will provide a framework for incorporating new developments in technology. The document can be used by on-scene coordinators, toxic waste managers, regulatory agencies, and researchers as it will provide a format for bridging the gap between research and development and field applications of in situ treatment techniques which are applicable to large quantities of hazardous waste contaminated soils.

APPROACH FOR IN SITU TREATMENT

Elements that are believed to be essential in a comprehensive approach to an in-situ treatment program are present in Figures 1 and 2. Figure 1 contains those elements related to the goals of in-situ

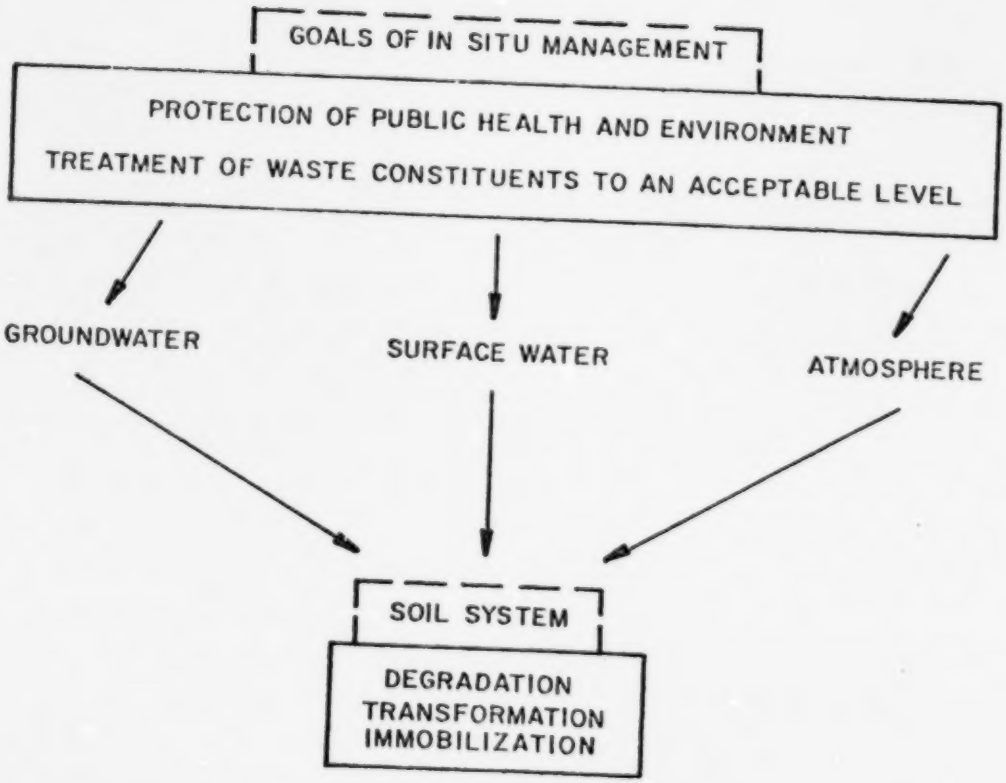

Figure 1. Elements related to the goals of in-situ treatment of hazardous wastes.

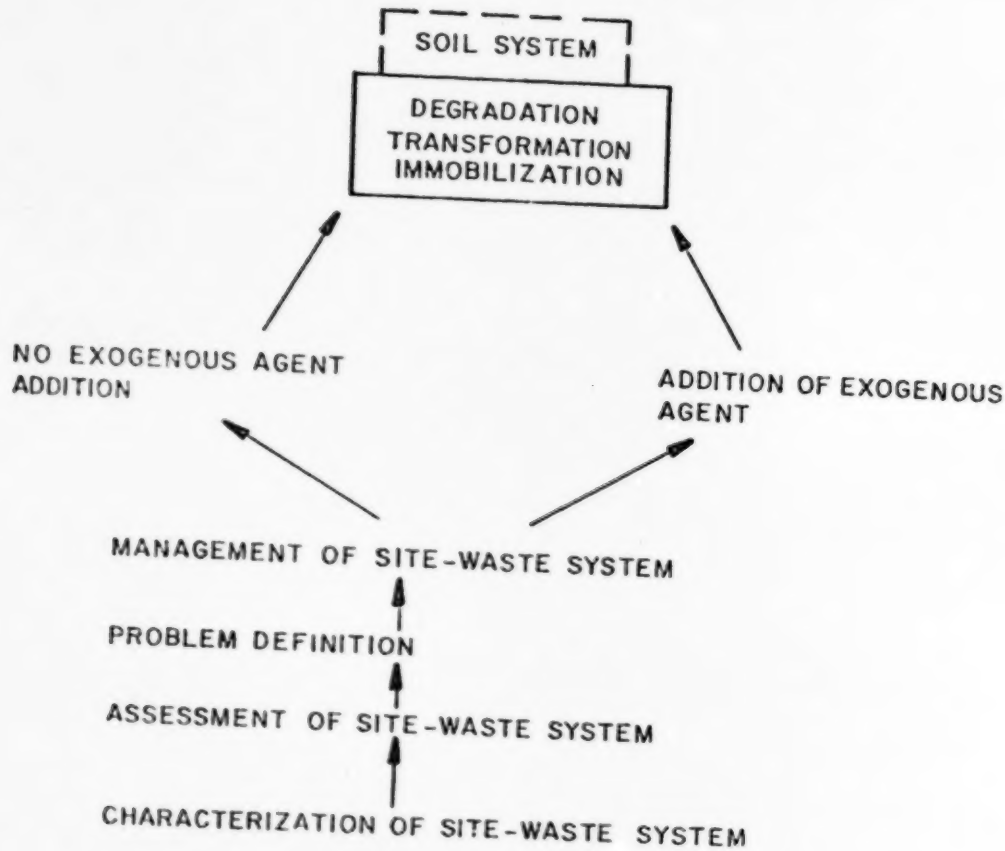

Figure 2. Steps required for accomplishing in-situ treatment.

treatment. These elements include: (1) reducing concentration of contaminants to an acceptable level and (2) protection of public health through control of transport pathways (leaching, runoff, volatilization) from terrestrial systems to the environment (groundwater, surface water, and atmosphere). Figure 2 contains the steps required for efficiently and cost-effectively accomplishing the goals of in-situ treatment. These elements include: (1) characterization of the site-waste system, (2) problem definition with respect to potential waste impact, (3) management of the site-waste system, and (4) soil treatment technique(s) selection and application including addition of a treatment agent(s), or augmentation of natural processes, for example, through amendment addition, or a combination of both approaches.

Characterization of the Site-waste System

Characterization and evaluation of the site-waste system is necessary in order to select treatment techniques that are appropriate and cost-effective. This phase of the methodology includes the following specific components: (1) assessment of site-waste-soil conditions, (2) role of sorption in determining the fate of waste constituents, (3) fate of constituents with respect to microbial processes in soil, (4) potential chemical reactions in the soil-waste matrix, and (5) assessment of potential volatilization of waste constituents from the soil-waste matrix. Each of these factors will influence the selection and application of treatment techniques for in-situ treatment.

Specific site and soil characteristics which need to be identified during site assessment for in-situ treatment management are summarized

in Table 1. The first aspect of site assessment with respect to in-situ treatment is to evaluate potential public health hazards due to off-site migration of hazardous compounds to ground and surface waters and transmission through air. The potential for migration, along with characteristics of the waste and the surrounding environment, indicate the degree of hazard the site poses. Secondly, the site must be evaluated in terms of its potential for decreasing the degree of hazard through degradation, transformation, and immobilization. Those site-soil conditions that may be managed to enhance these soil processes are indicated in Table 1. A third aspect of site characterization involves assessment of the site with regards to actual execution of in-situ treatment, for example, trafficability of the soil.

Soil sorption is perhaps the most important soil-waste process affecting the toxic and recalcitrant fractions of hazardous wastes. The influence of soil sorption on the extent and rate of leaching, and also on biological decomposition of these fractions must be understood and described in order to effectively use the sorption reaction as part of treatment processes. The relationship between immobilization of chemical constituents in soil systems, based on soil chemical properties, and chemical class, based on chemical structure, is summarized in Table 2. Generally, nonionic constituents of low water solubility and cationic constituents have low mobilities with respect to leaching potential. Acidic constituents at neutral and high pH values are most easily leached from soil systems.

Understanding the relationship between soil water content and extent of sorption of hazardous chemicals provides the hazardous waste manager with a process for controlling potential release and migration

Table 1.

Site and Soil Characteristics Identified as Important in In-situ Treatment

Site location/topography
Slope of site - degree and aspect
Soil, type, and extent
Soil profile properties
depth
boundary characteristics
texture*
amount and type of coarse fragments
structure*
color
degree of mottling
presence of carbonates
bulk density*
cation exchange capacity*
clay content
type of clay
pH*
Eh*
surface area*
organic matter content*
nutrient status*
microbial activity*
Hydraulic properties and conditions
depth to impermeable layer or bedrock
depth to groundwater*, including seasonal variations
infiltration rates*
permeability*(under saturated and a range of unsaturated conditions)
water holding capacity*
soil water characteristic curve
field capacity/permanent wilting point
flooding frequency
runoff potential*
aeration status*
Climatological factors
temperature*
wind velocity and direction

*Factors that may be managed to enhance soil treatment

Table 2

Leaching Potential of Chemicals in Soil Systems

Leaching potential	Chemical class								
	Nonionic			Ionic					
	water solubility			basic		cationic	acidic		
	high	med	low	low pH	neutral pH		low pH	neutral pH	
Low			X	X		X			
Medium		X			X		X		
High	X								X

of constituents through leaching. One commonly used isotherm that is used to describe the immobilization of organic constituents in soils is the Freundlich isotherm. This isotherm can be expressed as:

$$S = K C_N \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where K and N are constants,

S = amount of chemical associated with the solid phase, or the solid phase concentration (weight of chemical per weight of solid),

C = amount of chemical associated with the solution phase, or the solution phase concentration (weight of chemical per weight or volume solution).

The Freundlich isotherm relates the solid phase concentration to the solution phase concentration at equilibrium conditions.

The linear isotherm is an important isotherm which can be obtained from the Freundlich isotherm when N = 1. The linear isotherm may be expressed as:

$$S = k_d C \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where k_d is called the distribution coefficient. This form of the isotherm has been used for relatively low concentration of pesticides in soil systems.

The relationship between k_d, soil water θ, and percent adsorption of an organic chemical can be used to manage a soil system. This relationship may be expressed as:

$$\text{percent adsorbed} = k_d/(k_d + \theta) \quad \ldots\ldots\ldots\ldots (3)$$

where θ = soil moisture content (volume of water per weight of dry soil, and assuming density of water = 1.0 g per ml).

Figure 3 illustrates the extent of sorption (percent adsorbed) as a function of soil moisture content for different values of the distribution coefficient. From Figure 3 it is obvious that careful control of soil water content will determine, to a large extent, the relative immobilization of a given set of chemical constituents identified at a remedial site. Optimization of cost effective and efficient treatment may require a compromise between optimum soil moisture content for biodegradation versus sorption. Implications for specific treatment schemes will be discussed in the manual.

The organic carbon content of a soil appears to play a dominant role in influencing the distribution coefficient (k_d). Results from investigations of soil-hazardous and soil-nonhazardous organic interactions suggest that soil organic matter plays the most important role in adsorption of organic chemicals by soils.

The fate of metals (inorganic constituents) added to soil is controlled by a complex and dynamic system of physical, chemical, and biological reactions. Metals, unlike many hazardous organic constituents, cannot be degraded or readily detoxified. Toxic metals represent a long term threat in the soil environment. This threat can be reduced considerably if the heavy metals can be permanently immobilized by either chemical or physical methods.

Table 3 lists the concentration ranges of inorganic constituents in soils found at 436 field investigation team (FIT) sites. Also listed are the natural background levels of these constituents in un-contaminated soils. From the table it is seen that barium, cobalt, and vanadium concentrations at the FIT sites summarized were within background levels.

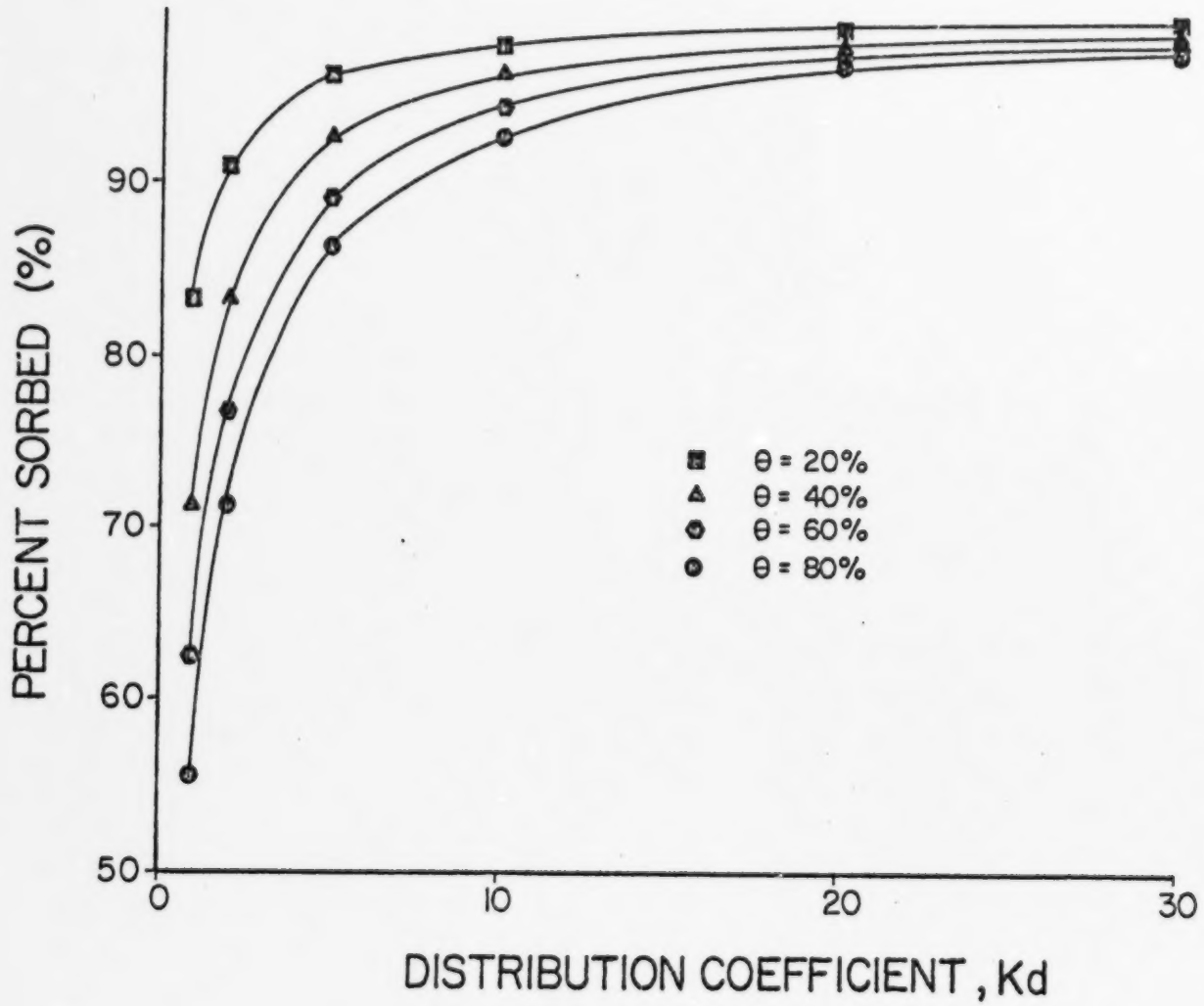

Figure 3. Extent of sorption as a function of soil moisture and k_d.

Table 3

Content of Various Elements in Uncontaminated[1] and Contaminated (FIT Sites) Soils

Element	Common Range for Soils (ppm)	Range at FIT Sites for Soils (ppm)
Sb	2-10	15*
As	1-50	0.02-11,700
Ba	100-3,000	0.02-0.2
Be	0.1-40	2-38
B	2-100	0.3*
Cd	0.01-0.70	0.3-118,300
Cr	1-1,000	0.04-136,000
Cu	2-100	2.2-186,300
Co	1-40	2.6*
Pb	2-200	0.16-466,000
Hg	0.01-0.3	0.04-83,200
Mo	0.2-5	322*
Ni	5-500	0.4-8.800
Se	0.1-2	0.9-1.3
Ag	0.01-5	1.2-18
V	20-500	0.04-2
Zn	10-300	0.03-38,000
F	104,000	110,000*

*one site reporting concentration

Source: Ecology and Environment, Inc. Field Investigations of uncontrolled hazardous waste sites. FIT Project EPA Contract #68-01-6056.

The chemistry of heavy metals in soils can be divided into two interdependent but separate categories: (1) solution chemistry and (2) interfacial chemistry. Factors affecting and controlling the behavior of inorganic constituents in soil systems will be considered in detail in the field guidance manual.

Microorganisms are highly effective in removing certain hazardous organic constituents from soil systems. Organic chemical decomposition in soil systems is a complex process which depends upon organic substance properties, soil properties, and environmental factors. The addition of exogenous toxic organic wastes to soil systems greatly increases the complexity of soil metabolic processes. This is partly because organisms are exposed to at least three different types of chemicals: (1) readily consumable substrates, (2) toxic constituents which may inhibit metabolic processes, and (3) non-readily consumable organics which may not be toxic, but which do not serve as sources of carbon and energy for cellular metabolism (cosubstrates).

Although results for degradation of hazardous waste constituents cannot be presented here in full, data are summarized for the polynuclear aromatic (PNA) class of organic priority pollutants in Figure 4. The data compiled by Sims and Overcash[2] represent results from the literature and from laboratory studies. General trends can be summarized as follows: (1) the initial rate of transformation increases with increasing initial soil concentration for a given PNA compound, (2) the initial rate of transformation decreases with increasing number of fused benzene rings within the class of PNA compounds.

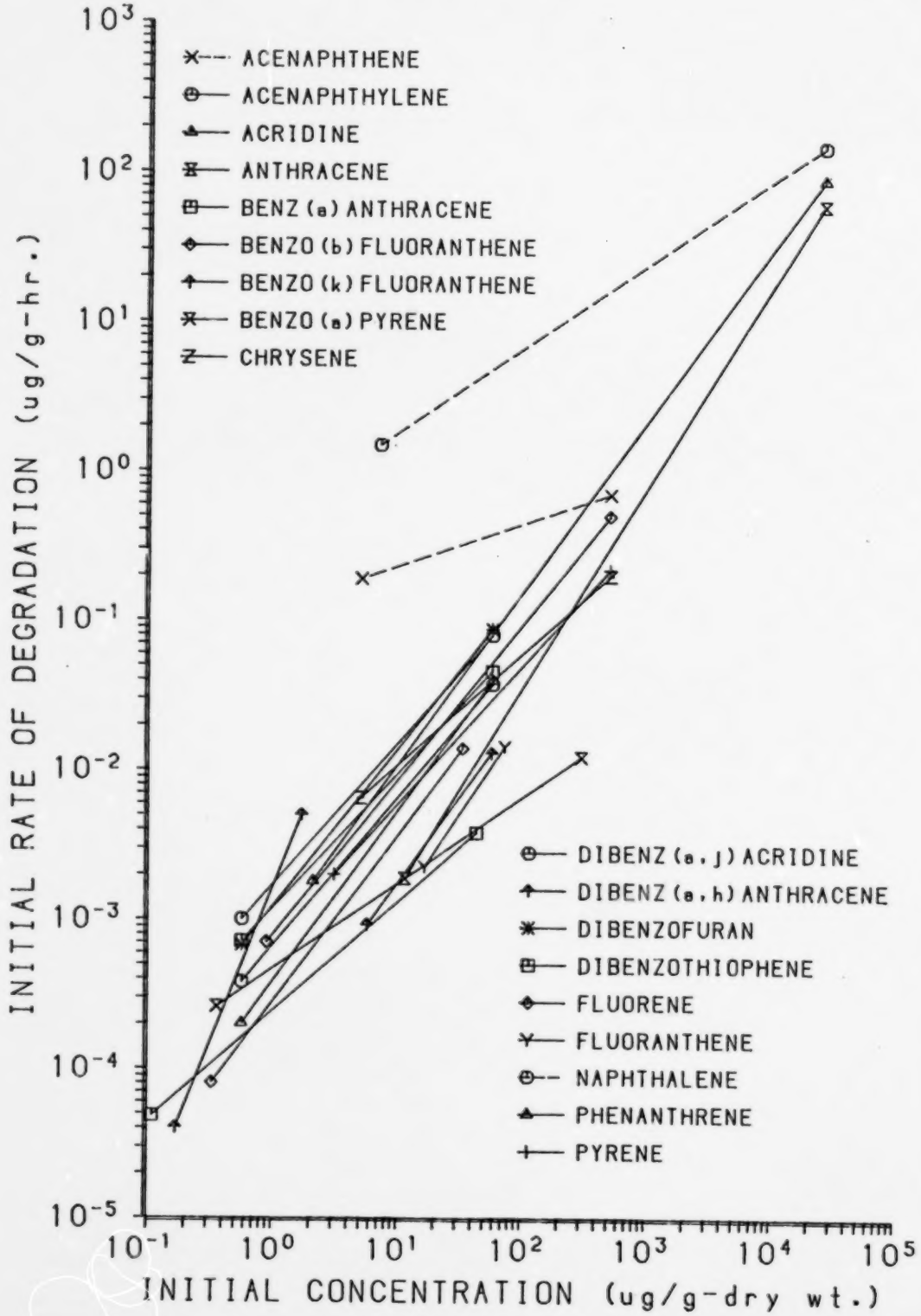

Figure 4. Rates of transformation of PNA compounds in soil as a function of initial soil concentration.

Several classes of chemical contaminants are considered concerning chemical-soil reactions and reactions resulting from addition of treatment agents to soil-waste systems. Only the solvent class of chemical contaminants is discussed here.

Available studies indicate that little information has been generated concerning the leaching behavior or effects of nonaqueous or aqueous-nonaqueous mixtures in terrestrial systems. However, assessment of hazardous waste sites has identified numerous organic solvents present that are not present as trace contaminants in an aqueous solvent.

Several recent studies have indicated that organic materials will react with clay minerals in soil systems to generally increase clay permeability[3,4,5,6,7]. Studies on the effects of solvents on clay permeability have been concerned with clay liner integrity in landfill sites. However, results from these studies have important implications for large quantities of hazardous waste contaminated soils, specifically with respect to soil structure and the effects of soil structure on leaching potential.

The effects of organic solvents on clay permeability of one soil having smecitite as the dominant clay mineral are presented in Table 4[4]. Smecitite clays were the most susceptible to permeability changes by organic solvents. General classes of organics, including acidic, basic, neutral polar, and neutral nonpolar are included. From Table 4 it is evident that most solvent organics increase permeability of clay minerals in soil systems. It is not known, at present, how dilute aqueous mixtures of organic solvents will affect the permeability of soils.

Table 4

Effect of Organic Solvent in Clay Permeability[4]

Chemical Class	Solvent	Effect on Permeability	Comment
Acid	Acetic acid	decrease	dissolution of clay
Base	Aniline	increase	100 fold for Lufkin* 10 fold for H.B.*
Neutral Polar	Acetone	increase	1000 fold for Lufkin 50 fold for H.B.
	Ethylene Glycol	increase	100 fold for Lufkin 4 fold for H.B.
Neutral Nonpolar	Xylene	increase	1000 fold for Lufkin 100 fold for H.B.
	Heptane	increase	similar to Xylene

* smectite clay

Volume I of the manual will include the methodology for choosing treatment techniques. Specific information needs and analysis, and endpoints obtained will be indicated with respect to: (1) characterization of the site-waste-soil system, (2) assessment of the site-waste system, (3) problem definition, and (4) management of the soil-waste-site system. Examples for using the methodology for specific site-soil-waste combinations will be reported in the field guidance manual.

Soil Treatment Technique(s) Selection and Application

Soil treatment is defined as a set of physical, chemical, and/or biological reactions, natural or induced, that accomplishes degradation, transformation, or immobilization of hazardous constituents in the soil system. The endpoint is to achieve acceptable levels of constituents in the soil solution.

Treatment involves two major approaches. A treatment agent (physical, chemical or biological) may be added to the soil-waste system to accomplish the objectives of treatment, or treatment may be accomplished through the augmentation of natural processes in the soil-waste system. Addition of an amendment to a soil-waste system may cause an increase in the rate, effectiveness, or extent of natural processes.

Physical, chemical, and biological treatment processes considered for in-situ treatment of hazardous waste contaminated soil are characterized and organized for presentation and evaluation according to the outline presented in Table 5.

A summary of variables that can be controlled in physical, chemical and biological treatment processes for in situ treatment

Table 5. In-situ Treatment Processes for Hazardous Wastes

I.	IDENTIFICATION
	A. Process fundamentals
	B. Information requirements
II.	EVALUATION
	A. Status of the technique
	B. Feasibility and effectiveness
III.	DESIGN
	A. Management variables
	B. Equipment needs
	C. Application methods
IV.	COST ANALYSIS
	A. Unit costs
	B. Other costs
V.	EXAMPLES AND SOURCES OF INFORMATION

including treatment agent addition and treatment augmentation, are presented in Table 6.

Based upon the information presented concerning the behavior, fate, and reactions of chemical constituents in soil systems, and treatment options available for in-situ treatment, a methodology is presented for choosing specific techniques to match site-waste-soil requirements. In order to determine cost effective, rational, and appropriate treatment techniques it is necessary to define the problem within the context of the treatment endpoints.

ACKNOWLEDGMENT

This work was funded by the U.S. Environmental Protection Agency Municipal Environmental Research Laboratory, Cincinnati, Ohio, under Contract 68-03-3113, Task 41. The authors wish to acknowledge the assistance and support of the project officer, Naomi Barkley. They also wish to thank the project staff, Dr. Darwin Sorensen, co-principal investigator, Dr. Jerry Jurinak, Dr. Dean Adams, Joan McLean, Judith Sims, Ramzi Mahmood, and the support staff at the Utah Water Research Laboratory. The contributions of Dr. Ryan Dupont, Utah Water Research Laboratory, are appreciated.

REFERENCES

1. Lindsay, W. L. Chemical Equilibria in Soils. John Wiley and Sons, New York, N.Y.

2. Sims, R. C., and Overcash, M. R. "Fate of Polynuclear Aromatic Compounds (PNAs) in Soil-Plant Systems". Residue Reviews, 88, 1983, 1-68.

3. Buchanan, P. N. "Effect of Temperature and Adsorbed Water on Permeability and Consolidation Cahracteristics of Sodium and Calcium Montmorillonite." Ph. D. Dissertation. Texas A & M University, College Station, Texas, 1964.

Table 6. Physical, Chemical, and Biological Treatment Processes Considered for In-situ Treatment

	Biological	Chemical	Physical	Photochemical
No Exogenous Agent	moisture modification nutrient addition analog enrichment pH adjustment aeration organic matter addition temperature adjustment	moisture modification (oxidation/ reduction) pH adjustment (hydrolysis) temperature adjustment	moisture modification pH adjustment	moisture modification volatilization
Exogenous Agent Addition	microorganism seeding genetic strains acclimated strains	oxidation ozone peroxides reduction sodium sulfide calcium sulfide sodium borohydride organic matter precipitation calcium oxide chelation	sorption activated carbon organic matter mineral addition	photosensitized sensitizers dyes

4. Anderson, D. C., and Brown, K. W. "Organic Leachate Effects on the Permeability of Clay Liners". Proceedings of the Seventh Annual Research Symposium. D. W. Schultz, ed. EPA-600/9-81-002b, 1981.

5. Anderson, D. C., Brown, K. W., and Green, J. "Organic Solvent Effects on the Permeability of Clay Soils." Land Disposal of Hazardous Wastes. EPA-600/9-82-002, 1982.

6. Brown, K. W., and Anderson, D. C. "Effects of Organic Solvents on the Permeability of Clay Soils." EPA-600/2-83-016, 1983.

7. Brown, K. W., Green, J., and Thomas, J. "The Influence of Selected Organics Liquid on the Permeability of Clay Liners." In: D. W. Schultz (ed.) Land Disposal, Incineration, and Treatment of Hazardous Waste. In Press. 1983.

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